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Journal of Polymer Science, Part B

Polymer Letters

Editorial Board: R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

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Journal of Polymer Science **Part B: Polymer Letters**

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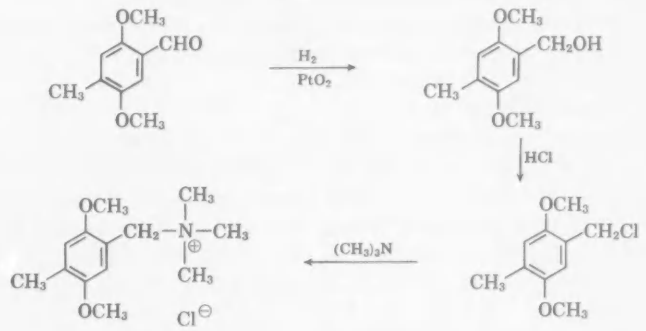
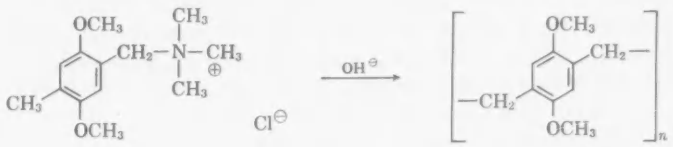
POLYMER LETTERS VOL. 1, PP. 117-119 (1963)

POLY-2,5-DIMETHOXY-p-XYLYLENE

A recent publication on the preparation of poly-2,5-dimethoxy-p-xylylene by reaction of phenyllithium with 2,5-dimethoxy-p-xylylene diiodide (1) prompts us to describe our preparation of this material by a different route. The reaction of p-methylbenzyltrimethylammonium quaternary salts with aqueous alkali has been reported to yield a poly-p-xylylene which is more soluble than that prepared by other methods (2). Accordingly we have prepared 2,5-dimethoxy-4-methylbenzyltrimethylammonium chloride by the following sequence.



Reaction of the quaternary salt with concentrated alkali readily gave poly-2,5-dimethoxy-p-xylylene as a white powder, softening at 235°C. It was insoluble in most organic solvents but was somewhat soluble in bromoform.



Reaction of the polymer with HBr in acetic acid gave poly-2,5-dihydroxy-p-xylylene as a brown powder. This material was insoluble in organic solvents as well as in 50% sodium hydroxide solution. In the latter solvent in the presence of oxygen, surface color changes were ob-

served reminiscent of the similar colors produced with 2,5-xylohydroquinone under similar conditions.

Experimental

2,5-Dimethoxy-4-methylbenzyl alcohol. A mixture of 54 g. of 2,5-dimethoxy-4-methylbenzaldehyde, 0.5 g. platinum oxide, and 0.1 g. ferrous sulfate in 175 ml. absolute ethanol was hydrogenated on a Parr shaker. The solvent was evaporated yielding 46 g. (85%) of the alcohol. The product was recrystallized from ligroin, m.p. 78°C.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.9; H, 7.7.
Found: C, 66.0; H, 7.8.

2,5-Dimethoxy-4-methylbenzyl chloride. A sample of the above alcohol (18.2 g.) was dissolved in 200 ml. of toluene and saturated with gaseous hydrogen chloride. The solution became turpid and the water layer was removed with a separatory funnel. Evaporation of the toluene left an oil which crystallized from ligroin, 13 g. (65%), m.p. 63°C.

Anal. Calcd. for $C_{10}H_{13}Cl\,O_2$: C, 59.8; H, 6.5; Cl, 17.7.
Found: C, 59.3; H, 6.6; Cl, 17.3.

2,5-Dimethoxy-4-methylbenzyltrimethylammonium chloride. Gaseous trimethylamine was bubbled into a solution of 13 g. of the benzyl chloride in 100 ml. of dry acetone for 10 min. A white solid crystallized which was hygroscopic, 15.5 g. (90%), m.p. 198°C.

Anal. Calcd. $C_{13}H_{22}Cl\,NO_2 \cdot H_2O$: C, 56.5; H, 8.7; N, 5.1; Cl, 12.8.
Found: C, 56.5; H, 8.5; N, 5.2; Cl, 12.8.

Poly-2,5-dimethoxy-p-xylylene. A solution of 50 g. sodium hydroxide in 75 ml. of distilled water was deaerated with nitrogen for 15 min. and heated to 90°C. To this solution was added a deaerated solution of 15 g. of quaternary salt in 30 ml. distilled water with stirring under a nitrogen atmosphere. The reaction was worked up after 1.5 hr. yielding 4.5 g. (50%) of a white material, softening point 235°C. It was insoluble in all solvents tried except bromoform.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.2; H, 7.3.
Found: C, 73.0; H, 7.3.

Poly-2,5-dihydroxy-p-xylylene. 2 g. of the dimethoxy polymer was suspended in a 50% mixture of bromoform and acetic acid. The mixture was heated on a steam bath for four days with periodic additions of gaseous hydrogen bromide. The product was insoluble, even in aqueous caustic.

The infrared spectrum, however, was very different from the dimethoxy polymer and typical of a hydroquinone derivative. The surface of the polymer in the presence of oxygen and alkali became green and finally brown, presumably due to the formation of oxidation products such as hydroxyquinone and quinone.

Anal. Calcd for $C_8H_8O_2$: C, 70.6; H, 5.9.
Found: C, 68.2; H, 5.9.

References

(1) Golden, J. H., J. Chem. Soc., 1961, 1604.
(2) Schaefgen, J. R., J. Polymer Sci., 41, 133 (1959).

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THE COPOLYMERIZATION OF 3-METHYLBUTENE-1 AND BUTENE-1

The most active Ziegler-Natta catalyst for the polymerization of bulk 3-methylbutene-1 is Stauffer A.A. $TiCl_3$ with aluminum triisobutyl. Even with this catalyst, however, runs at 60°C. lasting 4-5 hr. give rather low conversions and activities no higher than 25 g. polymer/g. $TiCl_3$/hr. In contrast, when small amounts (up to 5% by weight) of butene-1 are added to the monomer feed, high conversions are obtained and activities are in excess of 300. It appeared desirable to study the kinetics of and product composition from this reaction to understand this effect more fully.

Table I gives the results of two runs using 3-methylbutene-1 and C-14 labelled butene-1. The reactions were carried to approximately 25% conversion. At this stage all the butene-1 had been consumed.

The heptane soluble and heptane insoluble fractions differ in that the former are amorphous and the latter are crystalline. Since polybutene-1 prepared under these conditions is completely heptane soluble and poly-3-methylbutene-1 is almost completely insoluble (>97%), these fractions are almost certainly true copolymers and not mixtures of homopolymers. The soluble fractions are probably predominantly random copolymer while the insoluble fractions contain relatively long blocks of 3-methylbutene-1. Since butene-1 incorporation in the former fractions is about twice that in the corresponding insoluble fractions, two different types of catalytic sites must therefore be present, one of which favors random copolymerization while the other favors formation of block copolymers.

Bulk polymerization was too rapid to allow satisfactory kinetic runs to be made. Using heptane as a diluent, however, good first-order plots were obtained for the initial copolymerization. These break rather sharply and further growth of polymer results in a second first-order plot of lesser slope. As one would expect, this change of slope occurs when the butene-1 is virtually exhausted. Table II gives initial first-order rate constants for the copolymerizations and first-order constants for the reaction after butene-1 has been totally incorporated. While the rate of copolymerization is, indeed, higher than that of 3-methylbutene-1 homopolymerization, it is not sufficiently so to account for the much higher activities originally noted. The explanation of this apparent discrepancy is that the rate of homopolymerization falls after about one hour almost to zero whereas the copolymerizations continue to high conversions. 3-Methylbutene-1 homopolymer is extremely crystalline and highly insoluble. As polymerization proceeds it must form a lay[illegible] the catalyst surface which is impervious to monomer and conseq[illegible] the reaction ceases. A similar phenomenon has been observed in [illegible] Ziegler-Natta

TABLE I

Product Compositions from 3-Methylbutene-1, Butene-1 Copolymerizations

3-Methyl-1-butene, ml.	Butene-1-C-14, ml.	Total yield, g.	Yield heptane insoluble, g.	Counts/sec., total yield	Counts/sec., heptane insoluble	Wt.–% butene-1 in total yield	Wt.–% butene-1 in heptane insolubles	Wt.–% butene-1 in heptane solubles	Wt.–% butene-1 based on total incorporation
–	150	–	–	452	452	–	–	–	100
140	10	20.5	14.5	122	95	26.9	21.0	41.2	24.0
145.	5	21.2	17.5	28	23	6.2	5.1	11.4	5.7

TABLE II

Reaction Rates of 3-Methylbutene-1, Butene -1 Copolymerizations

3-Methyl-1-butene, ml.	Butene-1, ml.	Heptane, ml.	Initial rate, 10^3 hr. min.$^{-1}$	Final rate, 10^3 hr. min.
100	–	100	1.28	See text
100	4	96	2.50	1.64
100	5	95	5.55	2.34
100	6.5	93.5	7.20	2.45

Runs at 60°C., 0.4 g. A.A. $TiCl_3$. AlR_3: $TiCl_3$ 2:1

polymerization of styrene in aliphatic hydrocarbon media (1). The copolymer, being largely either noncrystalline or weakly crystalline, is more swollen by its own monomer and therefore does not inhibit polymerization. It is interesting that even after all the butene-1 has been consumed the further polymerization of 3-methylbutene-1 has a higher rate than the normal homopolymerization of this monomer. Apparently the initially formed random copolymer increases the solubility of the poly-3-methylbutene-1 block to which it is joined.

Reactivity ratios for this system were calculated from the data obtained in one run using C-14 labelled butene-1. The method of calculation was as follows: At zero time the monomer feed was of known composition M_1,M_2. The first aliquot at time, t_1, contains polymer from this feed with composition m_1,m_2. The monomer composition at time t_1 was now calculated to give a new feed M_1',M_2'. From the composition of the polymer obtained in the next aliquot at time t_2 (which contained the polymer existing at time t_1 plus that formed between times t_1 and t_2) m_1',m_2' the polymer composition from feed M_1',M_2' could be deduced. In this way, a series of points for a graphical solution of the copolymer equation was obtained (2). r_{45} (4=butene-1, 5=3-methylbutene-1) is 8.5 and r_{54} is 0.013.

These observed reactivity ratios are a composite of the individual ratios for the two kinds of catalytic sites. Interpretation of such reactivity ratios is less clear-cut than of those obtained for copolymerization in less complex systems. However, the degree to which the observed product $r_{45} \times r_{54}$ deviates from unity indicates that the relative reactivities of the two monomers toward the two chain ends is considerably different. This copolymerization is, therefore, unlike that of ethylene and propylene (3) and butene and propylene (4) where the products of the reactivity ratios are close to one. The difference may, in part, be due to steric hindrance between the 3-methylbutene-1 chain end and the incoming monomer.

References

(1) Burnett, G. M., and P. J. T. Tait, Polymer, 1, 158 (1960).
(2) Fineman, M., and S. D. Ross, J. Polymer Sci., 5, 269 (1950).
(3) Natta, G., A. Valvassori, G. Mazzanti, and G. Sartori, Chim e ind., 40, 896 (1958).
(4) Liebman, S., unpublished data.

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POLYMER LETTERS VOL. 1, PP. 125-126 (1963)

A COMMENT ON TSVETKOV'S THEORY OF FLOW BIREFRINGENCE OF POLYMER SOLUTIONS

According to the Tsvetkov's theory (1-3) the dynamo-optical constant of polymer solutions is expressed:

$$\lim_{\substack{q\to 0\\ c\to 0}} \left(\frac{\Delta n}{q\eta_0 c}\right) = [n]$$

$$= \frac{4\pi(n_s^2+2)}{45kTn_s}[\eta](a_1-a_2) + \frac{23.76\Phi M(n_k^2-n_s^2)^2}{45\pi\rho^2 n_s^3 N_A^2 kT}$$

$$= [n]_i + [n]_f \qquad (1)$$

where Δn is degree of flow birefringence, q is velocity gradient, and c is the concentration of polymer in solution. η_0 and $[\eta]$ are the viscosity of solvent and the intrinsic viscosity of the solution, respectively. n_s is the refractive index of solvent, n_k is the refractive index of polymer, M is its molecular weight, ρ is the density of polymer in solution, $(a_1 - a_2)$ is the optical anisotropy of the segment of a molecular chain. N_A is the Avogadro number, k is the Boltzmann constant, T is the absolute temperature, and the Flory constant is Φ. It is obvious that the second term of eq. (1), the form effect, should be negligible under the condition of $n_k = n_s$, and we obtain:

$$[n] = [n]_i \qquad (2)$$

Tsvetkov and Lyubina (4) derived the following equations in order to separate the form effect, $[n]_f$, and obtained the optical anisotropy of the segment of polymer chain, $(a_1 - a_2)$, from the values of dynamo-optical constant, [n], in the solutions:

$$(a_1 - a_2) = \frac{45kTn_0}{4\pi(n_0^2+2)^2}\frac{[n]_0}{[\eta]_0} \qquad (3)$$

where $n_k \neq n_s$,

$$[n]_f = [n] - [n]_i \qquad (4)$$

from eqs. (1), (3), and (4),

$$[n]_f = [n] - [n]_0 \frac{[\eta]n_0}{[\eta]_0 n_s}\left(\frac{n_s^2+2}{n_0^2+2}\right)^2 \qquad (5)$$

The optical anisotropy of the segment for a given polymer chain in a given solvent should not change, but except for the case of $n_k = n_s$ the values thus obtained using eqs. (3) and (5) are all incompatible with the theoretical expectations.

It has to be mentioned that the optical anisotropy of the segment of a polymer chain in solution, $(a_1 - a_2)$ value, is not the universal constant for various systems. We suggest that eq. (3) should be replaced by the following expressions:

$$[n]_0 = \frac{4\pi(n_0^2 + 2)^2}{45kTn_0} [\eta]_0(a_1 - a_2)_0 \tag{6}$$

Therefore

$$(a_1 - a_2)_0 = \frac{45kTn_0}{4\pi(n_0^2 + 2)^2} \frac{[n]_0}{[\eta]_0} \tag{6'}$$

$$(a_1 - a_2)_0 \neq (a_1 - a_2) \tag{7}$$

where the values of $[n]_0$, $[\eta]_0$, $(a_1 - a_2)_0$, and n_0 express the characteristic values of $[n]$, $[\eta]$, $(a_1 - a_2)$, and n_s, respectively, under the condition of $n_k = n_s$.

As described above, eqs. (3) and (5) quoted from Tsvetkov's theory are not qualified for derivation of the optical anisotropy of the segment of polymer chain in solutions when the refractive index of the solvent differs from that of the polymer.

References

(1) Tsvetkov, V. N., and E. V. Frisman, Acta Physicochim., U.S.S.R., 20, 61, 363 (1945).

(2) Tsvetkov, V. N., and E. V. Frisman, Dokl. Acad. Nauk. SSSR, 97, 647 (1954).

(3) Tsvetkov, V. N., J. Polymer Sci., 23, 151 (1957).

(4) Tsvetkov, V. N., and S. Ya. Lyubina, Vysokomolekul. Soedin, 1, 857 (1959).

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INFRARED AND X-RAY STUDIES OF POLY-γ-METHYL-l-GLUTAMATE SPHERULITE

To our knowledge, the only polypeptide from which spherulites have been grown is fibroin (1).

We have however recently succeeded in growing spherulites of poly-γ-methyl-l-glutamate (PMLG) from a chloroform solution (2), and we wish to report the results of the examination of these spherulites by infrared spectroscopy and x-ray diffraction.

PMLG was polymerized by the N.C.A. method in chloroform solution, with triethylamine as initiator. The molecular weight of the PMLG thus obtained was about 370,000, as determined by viscometry.

For making thin films of PMLG, the chloroform solution (0.5-2%) was left standing for two or three months after polymerization, then poured onto glass plates. The solvent was allowed to evaporate very slowly in an atmosphere of chloroform vapor. Using this method, we obtained thin films containing spherulites with diameters up to 2 mm.

Apparently, the ageing time and the type of solvent are the important factors in making spherulites. Chloroform seemed to us to be the best solvent; however, if the solution was not aged after polymerization, we could not obtain spherulites. With only one month's ageing, we obtained small imperfect spherulites; but with two months or longer, large spherulites were grown.

Figure 1 is the polarization microscopic photograph of one of these spherulites. Its diameter is about 0.9 mm. and its thickness is about 7 μ. It exhibits the typical black cross under crossed Nicols, and has a positive birefringence of 7×10^{-3}. This value of birefringence is about one third of that of well-oriented fibers which have an alpha-helical structure.

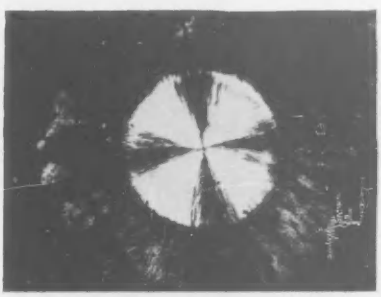

Fig. 1. The spherulite of PMLG under crossed Nicols.

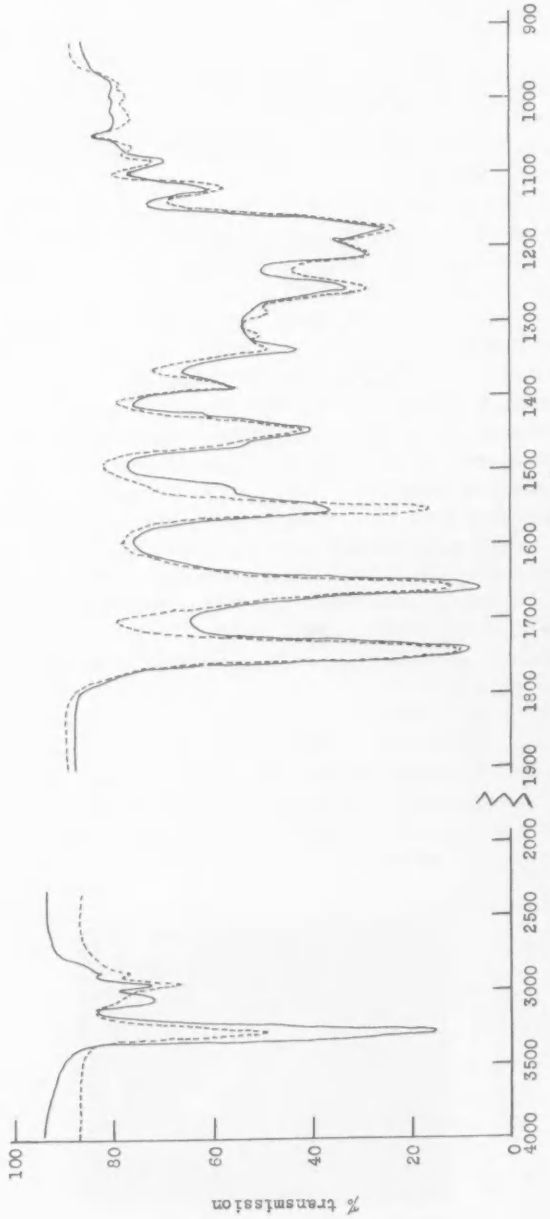

Fig. 2. Infrared absorption spectrum of the PMLG spherulite: (———) electric vector parallel to the radius; (- -) electric vector perpendicular to the radius.

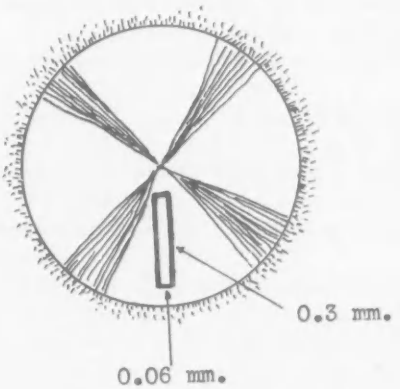

Fig. 3. The specimen used for the infrared spectrum (Fig. 2) (the black fringed rectangular part).

An infrared spectrum of this spherulite is shown in Figure 2.

It was taken with a Perkin-Elmer Model 85 Infrared Microscope in connection with their Model 13 Infrared Spectrophotometer. The specimen was obtained from the small rectangular area shown in Figure 3. The size of this selected area is 0.3 × 0.06 mm., and the longer side lies parallel to a radius of the spherulite.

A silver chloride polarizer was used for obtaining the polarized spectrum. The solid curve in Figure 2 represents the transmission with the

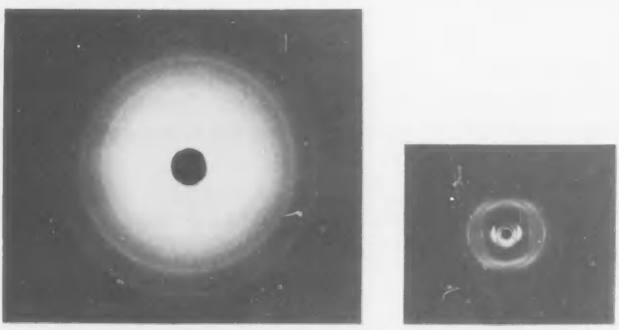

Fig. 4. X-ray diffraction photograph of the spherulite. (a) focussing at the center, taken by ordinary camera. (b) focussing at circumference, taken by micro camera.

electric vector parallel to the longer side of the specimen. The broken curve represents that with the electric vector perpendicular to the longer side of the specimen.

The N-H streching bands at 3280 and 3060 cm.$^{-1}$ show parallel dichroism.

The Amide-I band appears at 1653 cm.$^{-1}$, and also has parallel dichroism.

The Amide-II band at 1545 cm.$^{-1}$ shows strong perpendicular dichroism, and a weak parallel dichroic band appears at 1514 cm.$^{-1}$.

The Amide-III band appears at 1254 cm.$^{-1}$ with perpendicular dichroism.

The frequencies and the dichroism of the above-mentioned bands suggest that the PMLG molecules have an alpha-helical conformation in the spherulite (3,4), and the helical axes lie almost radially.

Furthermore, the Amide-V band appears at 617 cm.$^{-1}$ in the KBr region, and this band position is the characteristic of the alpha helical conformation (4).

But the dichroic ratios of these infrared bands are not sufficiently large to allow us to state with certainty that the helical axes are completely radially distributed.

Additional information obtained by x-ray diffraction as set out below confirms the conclusions which we have drawn from the infrared spectra.

The x-ray beam was focussed at either the center or the circumference of the spherulite using an ordinary camera or a micro camera. Figure 4a is an x-ray diffraction photograph of the center of the spherulite. Figure 4b is a circumferential photograph using a micro camera.

As seen in Figure 4b, the diffraction pattern is a typical fiber pattern. Some spacings obtained from the photographs agree very well with those of Bamford et al. (5), which were obtained from an alpha-helical film. From our x-ray diffraction results, we have estimated that the alpha-helical axes in the spherulite are in general along the radii.

However, it should be noted that the arcs in the x-ray diffraction photograph are rather broad, indicating imperfect orientation, consequently we can only conclude with certainty that many of the alpha helices are aligned in the radial direction.

We wish to acknowledge our thanks to The Aji-no-moto Company for their kindness in supplying the PMLG.

References

(1) Sobue, H., and H. Ishikawa, J. Chem. Soc. Japan, Ind. Chem. Sect., 64, 1320 (1961).

(2) Ishikawa, S., and T. Kurita, ibid., 65, 834 (1962).

(3) Miyazawa, T., and E. R. Blout, J. Am. Chem. Soc., 83, 712 (1961).

(4) Masuda, Y., T. Miyazawa, and J. Noguchi, The 15th Annual Meeting of Chem. Soc. of Japan, Kyoto, 1962.
(5) Bamford, C. H., et al., Synthetic Polypeptides, Academic Press, New York, 1956, p. 242.

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CLUSTERING OF WATER IN POLYMERS

An equation for determining the degree of clustering in a two-component mixture has been derived by Zimm (1) and applied to mixtures of polymers and solvents by Zimm and Lundberg (2). The power of this approach lies in giving a direct measurement of nonrandom mixing without the use of any preconceived model. Since the properties of a mixture will depend on the distribution of its components in space, this is important information to have.

The probability that the molecules i and j are at the positions (i,j) within the range d(i) and d(j) is given by

$$(1/V^2)F_2(i,j)d(i)d(j)$$

where $F_2(i,j)$ is the molecular pair distribution function. The cluster integral G_{11} where molecules i and j are of type 1 is defined by

$$G_{11} = (1/V) \int\int [F_2(i,j) - 1]\, d(i)d(j)$$

The mean number of type 1 molecules in the neighborhood of a given type 1 molecule in excess of the mean concentration of type 1 molecules is $\phi_1 G_{11}/v_1 = c_1 G_{11}$ where ϕ_1, v_1, and c_1 are the volume fraction, partial molar volume, and molar concentration of component 1, respectively. The addition of a type 1 molecule to the system makes a volume equal to G_{11} available to other type 1 molecules. In an ideal solution, it excludes its own volume to other molecules, and $G_{11}/v_1 = -1$.

The following expressions have been derived by Zimm (1) neglecting a small term containing the compressibility.

$$\frac{\phi_1 G_{11}}{v_1} = c_1 G_{11} = \phi_2 \left(\frac{\partial \ln \phi_1}{\partial \ln a_1} \right)_{p,T} - 1 \qquad (1)$$

$$\frac{G_{11}}{v_1} = -\phi_2 \left(\frac{\partial (a_1/\phi_1)}{\partial a_1} \right)_{p,T} - 1 \qquad (2)$$

The following equation is obtained by rearranging eq. 21 of Kirkwood and Buff (3) assuming that v_1 does not depend on a_1.

$$\left(\frac{\partial \ln \phi_1}{\partial \ln a_1} \right)_{p,T} = 1 + c_1 (G_{11} - G_{12}) \qquad (3)$$

From this one obtains $c_1 G_{12}$, the mean number of type 1 molecules in

TABLE I

Sorption Isotherms

Polymer	Reference
Cellulose	J. L. Morrison and M. A. Dzieciuch, Can. J. Chem., 37, 1379 (1959).
Keratin	J. L. Morrison and J. F. Hanlan, Proc. Intern. Cong. Surface Activity, 2nd, London, 2, 322 (1957).
Collagen	H. B. Bull, J. Am. Chem. Soc., 66, 1499 (1944).
Serum albumin	H. B. Bull, op. cit.
Egg albumin (lyophilized)	H. B. Bull, op. cit.
Nylon 66, fibers	H. B. Bull, op. cit.
Nylon 66, annealed films	H. W. Starkweather, Jr., J. Appl. Polymer Sci., 2, 129 (1959).
Polyvinyl acetate	L. J. Thompson and F. A. Long, J. Am. Chem. Soc., 76, 5886 (1954).
Polymethyl methacrylate	G. M. Brauer and W. T. Sweeney, Modern Plastics, 32, 138 (May 1955).

the neighborhood of a point occupied by a type 2 molecule in excess of the mean concentration of type 1 molecules.

$$\frac{\phi_1 G_{12}}{v_1} = c_1 G_{12} = -\phi_1 \left(\frac{\partial \ln \phi_1}{\partial \ln a_1} \right)_{p,T} = \left(\frac{\partial \phi_2}{\partial \ln a_1} \right)_{p,T} \qquad (4)$$

A tendency for type 1 molecules to cluster is revealed by values of G_{11}/v_1 greater than -1. Some clustering is expected for vapors sorbed in polymers, because the polymer segments must occupy adjacent sites (2,4). Zimm and Lundberg (2) found that G_{11}/v_1 is near $+1$ for the systems benzene-rubber and toluene-polystyrene. This is also true for water-collagen near saturation. At low relative humidities, G_{11}/v_1 is strongly negative for this system.

Cluster integrals for water sorbed in a number of polymers were calculated from sorption isotherms from the references listed in Table I. The effect of correcting for changes in total volume on mixing on $c_1 G_{11}$ was calculated for nylon 66 and cellulose and found to be negligible. The contribution to G_{11}/v_1 of the term involving the compressibility was about .03 or less, and this was also neglected. Excluding the crystalline portions of nylon 66 from the system had very little effect on the values of $c_1 G_{11}$.

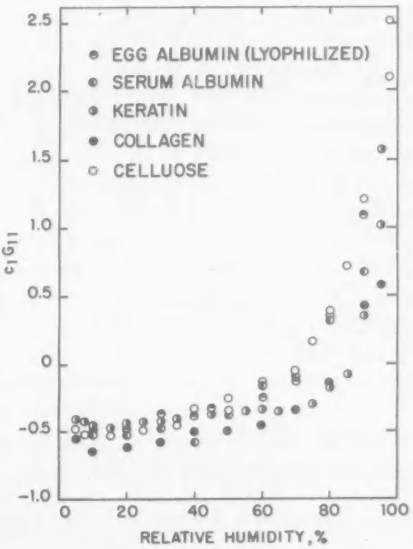

Fig. 1. Clustering of sorbed water in cellulose and proteins.

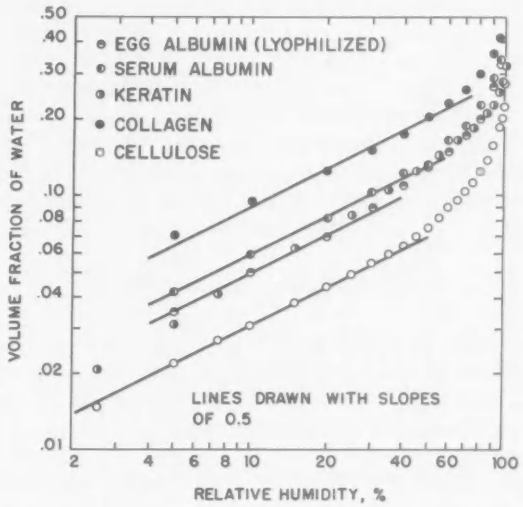

Fig. 2. Logarithmic plot of volume fraction of sorbed water vs. relative humidity.

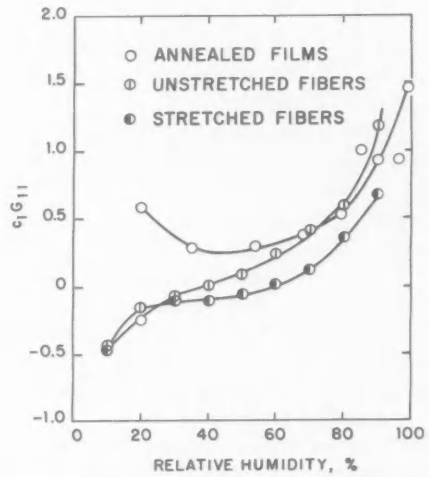

Fig. 3. Clustering of sorbed water in nylon 66.

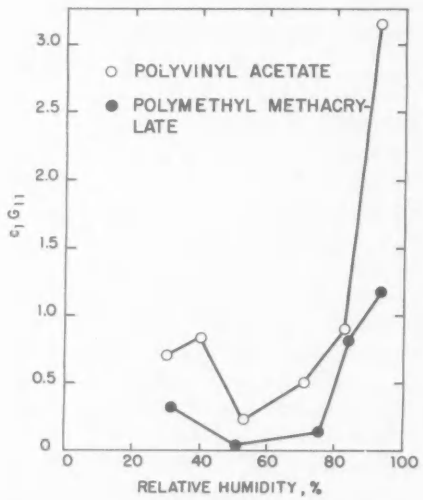

Fig. 4. Clustering of sorbed water in vinyl polymers.

Cellulose and Proteins

The dependence of c_1G_{11} on relative humidity for cellulose and a number of proteins is shown in Figure 1. In these cases, d ln ϕ_1/d ln $a_1 \cong 0.5$ up to about 20% relative humidity, and $c_1G_{11} \cong -0.5$. The amount of water absorbed is proportional to the square root of its partial pressure (Fig. 2). This dependence is also found for the sorption of hydrogen in palladium where it is attributed to dissociation (5). Since this relationship extends up to about 7% water by volume for several systems, this is not very plausible for the systems considered here. Moreover, there is some evidence that the slopes in Figure 2 increase at the lowest humidities and that there is a corresponding upturn of the points in Figure 1. This sort of behavior occurs when there is chemical or physical association between the two components in the mixture (6).

On the basis of eqs. (1) and (4), it is possible to make the following statements about the water absorbed in cellulose and proteins at low humidities.

(1) The number of water molecules in the neighborhood of a given water molecule is about 0.5 less than that expected from the mean concentration of water.

(2) One-half of the volume of a water molecule is excluded to water in the neighborhood of a point occupied by a polymer segment. This follows from eq. (4) when both sides are divided by ϕ_1. Since it was expected that the volume of the polymer would be excluded, this means that water-polymer contacts are favored.

As the relative humidity is increased, c_1G_{11} rises slowly and remains negative up to 70-85% R.H. At higher humidities, c_1G_{11} increases rapidly and passes a value of +1 near 90% R.H.

Since c_1G_{11} is the mean number of water molecules near a given water molecule in excess of the mean concentration, the mean size of the clusters is $c_1G_{11} + 1$. Thus, the size of the clusters is increasing rapidly near saturation. This is consistent with observations that the partial molar heat and entropy tend toward zero (7).

Nylon and Vinyl Polymers

The dependence of c_1G_{11} on relative humidity for nylon 66 is shown in Figure 3. The stretched and unstretched fibers studied by Bull resemble proteins in that c_1G_{11} approaches −0.5 at 0% R.H. and shows substantial clustering at high humidities. In annealed films this high humidity behavior is also found, but c_1G_{11} remains positive at all humidities and rises below 35% R.H. where the polymer is below a viscoelastic transition at room temperature.

Polyvinyl acetate and polymethyl methacrylate are similar to annealed nylon 66 in their behavior. In these cases, shown in Figure 4, the clus-

tering of the water molecules as evidenced by c_1G_{11} is at a minimum near 50% R.H.

References

(1) Zimm, B. H., J. Chem. Phys., 21, 934 (1953).
(2) Zimm, B. H., and J. L. Lundberg, J. Phys. Chem., 60, 425 (1956).
(3) Kirkwood, J. G., and F. P. Buff, J. Chem. Phys., 19, 774 (1951).
(4) Zimm, B. H., Rev. Mod. Phys., 31, 123 (1959).
(5) Glasstone, S., Textbook of Physical Chemistry, 2nd ed., Van Nostrand, New York, 1946, p. 785.
(6) Hildebrand, J. H., and R. L. Scott, The Solubility of Electrolytes, 3rd ed., Reinhold, New York, 1950, pp. 174-185.
(7) Dole, M., and A. D. McLaren, J. Am. Chem. Soc., 69, 651 (1947).

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DEGREE OF CRYSTALLINITY OF BLENDED POLYETHYLENE

Two kinds of polyethylene, PE, one of high pressure and the other of low pressure type, were blended and the degree of crystallinity (DC) was determined by different methods of density, infrared absorption (IR), and nuclear magnetic resonance (NMR) measurements. The high pressure PE used here is Alathon 20, and the low pressure one is Hi-Zex 3000, manufactured by Mitsui Petrochemical Industries, Ltd. Blended samples were prepared as follows: Two samples of PE in pellet form were taken at the ratios described in Figure 1, fused at 160–165°C. in an extruder, pushed out to water, and pelletized. This procedure was repeated again for each sample.

Density measurements were made by the ASTM method (1), and the intensities of IR spectra were compared at 730 cm^{-1} (2). The NMR method is same as that described in the literature (3).

The following features are deduced from the results of measurements shown in Figure 1.

(1). Additivity holds for the DC values obtained by each of the three methods.

(2). The DC magnitudes obtained depend upon the method used and they take the following relation for each sample: NMR > IR > Density.

As seen in Figure 1, the values of the density determinations are parallel to those of the IR, whereas those of the NMR are not parallel. An x-ray method was also applied to some of the samples, and showed a closer relation to the NMR data than the IR and density measurements. The additivity rule holds for the average molecular weights obtained by

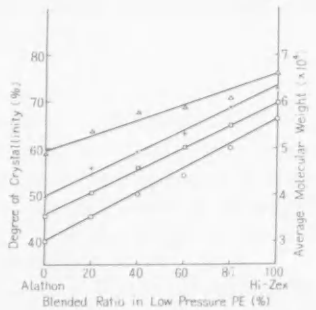

Fig. 1. Degree of crystallinity and average molecular weight of a blended polyethylene: (□) degree of crystallinity by density; (+) by IR; (Δ) by NMR. (○) Average molecular weight.

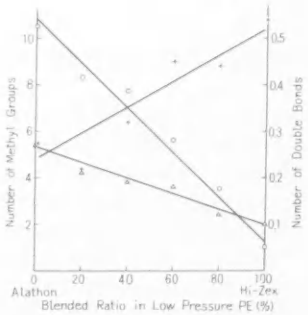

Fig. 2. Chemical structure of a blended polyethylene: (○) number of methyl groups, (Δ) number of vinylidene groups, (+) of total double bonds per 1000 carbon atoms.

viscosity measurements. Figure 2 shows the IR intensities for methyl groups and double bonds. They also obey the additivity rule.

The authors' thanks are due to Mr. Tsutomu Tanaka of Mitsui Petrochemical Industries, Ltd., for the supply of the blended samples and for help in the IR and density measurements.

References

(1) ASTM D 792-50.

(2) Stein, R. S., and G. B. B. M. Sutherland, J. Chem. Phys., 21, 370 (1953); 22, 1993 (1954).

(3) Wilson, C. W., III, and G. E. Pake, J. Polymer Sci., 10, 503 (1953); idem., J. Chem. Phys., 27, 115 (1957).

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EFFECT OF OXIDATION ON POLYETHYLENE MORPHOLOGY

Introduction

The rate of oxygen uptake in solid polyethylene during oxidation was observed to be inversely proportional to the per cent crystallinity (1). This indicates that only the amorphous regions of semicrystalline polyethylene are sensitive to oxygen attack.

In order to corroborate this observation, two polyethylene samples of different crystallinity content were exposed to oxidizing conditions over a period of 400 hr. and examined at intervals by infrared spectroscopy.

Experimental

All spectra were recorded on a Perkin-Elmer Model 21 Spectrometer. The frequency (abscissa) scale of the spectrometer was expanded 4× to increase the accuracy of the quantitative measurements. The samples were Marlex 6000, Type 5, a linear, highly crystalline polyethylene of density 0.96 produced by Phillips Chemical Company and DYNK, a branched polyethylene of density 0.92 produced by Union Carbide Plastics Company. The samples were films microtomed from melted and then resolidified polymers. Neither sample contained antioxidants. They were oxidized by exposing them to oxygen at 100°C. under controlled conditions (1).

Discussion and Results

Although the absorbance ratio of the 1303/720 $cm.^{-1}$ bands is sometimes used (2) to measure "infrared crystallinity," (3) the absorbance ratio R, ($R = A_{730\ cm.^{-1}}/A_{720\ cm.^{-1}}$) of the 730 and 720 $cm.^{-1}$ components of the methylene rocking doublet was used here.

The 730 $cm.^{-1}$ component of this doublet is associated with the $-CH_2$ groups in the crystalline regions of the polymer, and the 720 $cm.^{-1}$ component is due to the $-CH_2$ groups in the amorphous phase with some contribution from the crystalline phase. However, for our purpose, i.e., following the relative changes in the "infrared crystallinity" in these samples, no corrections were required.

Thus, in the spectrum of the highly crystalline Marlex, the components of the 730/720 $cm.^{-1}$ doublet are nearly of equal intensity, whereas in the less crystalline DYNK (~ 60% crystalline) the 730 $cm.^{-1}$ component is always considerably weaker than the 720 $cm.^{-1}$ band depending on the amorphous content of the particular sample.

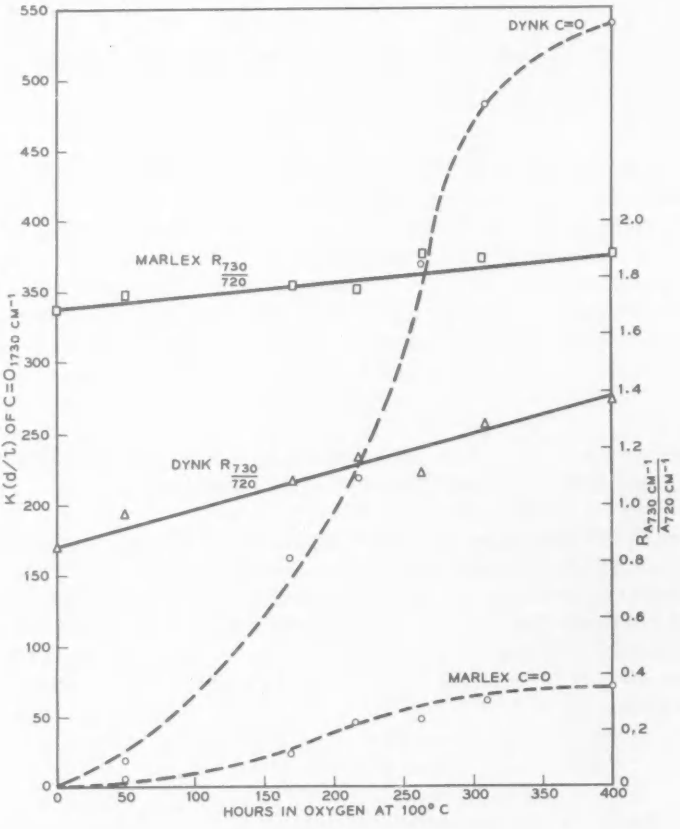

Figure 1.

The absorbance ratio ($R = A_{730\ cm.^{-1}}/A_{720\ cm.^{-1}}$) of the 720-730 $cm.^{-1}$ bands is plotted versus exposure time in Figure 1. Here we see that in both samples the 730/720 $cm.^{-1}$ ratio increases with exposure time, indicating an apparent increase in crystallinity during oxidation. A comparison of $R_{730\ cm.^{-1}/720\ cm.^{-1}}$ slopes (Marlex = .00047; DYNK = .00147) shows that there is a greater rate of apparent crystallinity increase in the DYNK sample than in the Marlex sample. Subsequent tests in nitrogen at 100°C. for 400 hr. showed this change is not due to an annealing effect.

Also shown in Figure 1 is the relative degree of oxidation that occurs in both samples. This is represented by the extinction coefficient K (K = d/l where d is absorbance and l is path length) of the –C=O group

at 1730 cm.$^{-1}$ which is plotted versus exposure time. In the semicrystalline DYNK, the rate of –C=O formation increases rapidly, particularly after approximately 100 hr. exposure when the rate increases sharply upward. In the highly crystalline Marlex, however, the formation of –C=O is considerably slower with no sharp increase, even during the autocatlytic phase after 100 hr.

Conclusion

The apparent increase in crystallinity during oxidation is attributed to the formation of –C=O, –OH, –OOH, etc., groups that form in the amorphous regions replacing the $-CH_2$ groups in the amorphous region, thus reducing their concentration. The reduction of these $-CH_2$ groups weakens the intensity of the 720 cm.$^{-1}$ band. This in turn increases the ratio, $R = A_{730\ cm.^{-1}}/A_{720\ cm.^{-1}}$ which results in the apparent crystallinity increase. Actually, there is no increase in crystalline regions as such (nor of the 730 cm.$^{-1}$ component), but the ratio of crystalline material to true (i.e., unoxidized) amorphous regions does increase. Thus, the weakening of the 720 cm.$^{-1}$ component is indicative of the sensitivity of the amorphous regions to oxygen attack.

Additional support for this observation is provided by comparing the oxidation resistance of the two similarly exposed samples. In the semicrystalline DYNK, the relatively rapid increase in –C=O formation is attributed to the greater amount of oxygen susceptible amorphous regions in this sample. In the highly crystalline Marlex, however, the rate of –C=O formation is considerably suppressed due to the higher ratio of oxygen-impervious crystalline regions.

This infrared evidence, therefore, shows that oxygen attack occurs principally in the amorphous regions of polyethylene in the solid state.

References

(1) Hawkins, W. L., W. Matreyek, and F. H. Winslow, J. Polymer Sci., 41, 1 (1959).

(2) Tobin, M. C., and M. J. Carrano, J. Polymer Sci., 24, 93 (1957).

(3) Wood, D. L., and J. P. Luongo, Modern Plastics, 38, 132, March 1961.

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ANIONIC POLYMERIZATIONS VIA THE MICHAEL REACTION

The Michael reaction consists of the addition of one activated electron-donating group (the donor) to a conjugated, polarized double bond system (the acceptor). The reaction often gives high yields, is reversible, and favored by low temperatures. A wide variety of solvents, donors, acceptors, and catalysts have been used in the past 75 yr. since the reaction was first used by Arthur Michael in 1887 (1); an extensive review has recently been published (2).

The separate steps in the Michael reaction correspond to the initiation and termination steps in anionic polymerizations (3). In some cases the reaction product may act as an activated donor and add to another acceptor molecule, forming a polymer. Examples of such poly-Michael reactions are the polymerizations of acrylates (4) and methacrylates (5) and other electron-deficient terminal olefins in the presence of anionic initiators. In principle, one might expect polymerization to be more general than has been reported and perhaps to take place with 1,2-disubstituted olefins for there are no absolute steric restrictions on the initial addition; for example, ethylmalonate adds to ethyl cinnamate and ethyl cyanoacetate adds to ethyl-β,βdimethylacrylate. It does not appear likely that a second addition would involve more steric hindrance. Nevertheless, ethyl crotonate gives only a dimer when allowed to react in refluxing ether with sodium ethoxide (13), at lower temperatures some trimer is formed too (14). Crotononitrile is polymerized with sodium ethoxide to dimers as the dominating product, with the formation of small amounts of trimers and higher polymers (14). However, β-nitrostyrenes (6-8) and 1-nitropropene (9-11) are reported to give high yields of polymeric materials on reaction with (presumably) anionic initiators, and alkylidene cyanoacetic esters are reported to polymerize in the presence of alkali (12).

We have therefore investigated the possibility of preparing polymers by Michael reactions of 1:2-disubstituted unsaturated monomers. We can fully confirm the reported polymerizations of β-nitrostyrene and 1-nitropropene with anionic initiators, but the polymers were largely insoluble in all solvents investigated, and therefore were not further investigated. Our results indicate, however, that the easy polymerization of these unsaturated nitro compounds are exceptional, and that monomers with a 1:2-disubstituted double bond conjugated with carbonyl or nitrile do not generally give high polymers by a poly-Michael reaction. We have investigated 15 monomers of this type under a wide range of possible polymerization conditions (Table I) using dimethylsulfoxide, toluene, dimethylformamide, and tetrahydrofuran as solvents, and isobutylmagnesium bro-

TABLE I

Solvent-Monomer-Catalyst Combinations Investigated

Monomer	Toluene	DMSO	DMF	THF	Bulk
Dimethyl maleate	Grignard[g] BuLi[d]	BuLi[a,e]			BuLi[a,d]
Dimethyl fumarate		BuLi[e]			
Diethyl maleate	Grignard[g]	Grignard[e]			BuLi[d,e]
Diethyl fumarate	Grignard[g] BuLi[d,g]	Grignard[e] BuLi[e]	BuLi[d]		BuLi[d]
Maleic anhydride	Grignard[g]	BuLi[e]	BuLi[d]		
Fumarodinitrile	Grignard[b,f,g]	Grignard[b,e]	BuLi[b,d]		
Methyl crotonate	BuLi[d,g]		BuLi[d]		BuLi[d,e]
Ethyl cinnamate	Grignard[g] BuLi[d,g]	Grignard[e] BuLi[e]			BuLi[d,e]
Ethyl-4-methoxycinnamate	BuLi[d,e]	BuLi[e]	BuLi[d]	BuLi[f]	

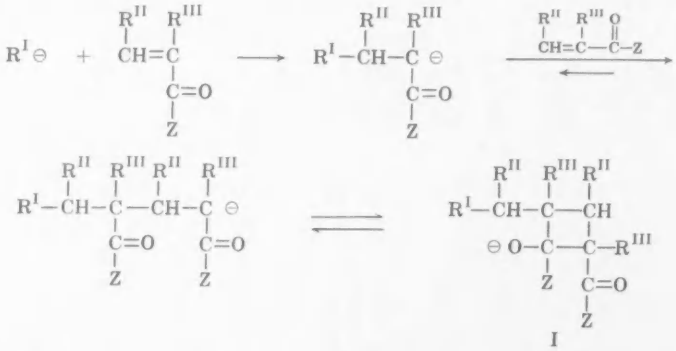
Ethyl-α-acetylcinnamate	BuLi[d]		BuLi[d]		
Ethyl-α-acetyl-4-methoxycinnamate	BuLi[d,g]		BuLi[d]	BuLi[g]	
Ethyl-α-cyanocinnamate	BuLi[d]		BuLi[d]	NaOMe[f]	
Ethyl-α-cyano-4-methoxycinnamate	BuLi[d,g]	BuLi[e]			
Ethyl-α-acetylcrotonate	BuLi[d,g]	BuLi[e]	BuLi[d]		
Ethyl-2-cyano-4-methylpent-2-enoate		BuLi[e]	BuLi[c,d] NaOMe[c,g]		BuLi[d]

[a]Isomerizes to dimethyl fumarate
[b]Decomposes
[c]Gives a crystalline isomer, tentatively formulated as ethyl-2,2-dimethyl-1-cyano-cyclopropane-1-carboxylate

Conditions: [d]–20°C., 3-6 mo.
[e]Ambient, 4-6 hr.
[f]0°C., 4-6 hr.
[g]–40 to –60°C., 4-6 hr.

mide, n-butyllithium, and sodium methoxide as initiators, and temperatures ranging from ambient to −60°C. and reaction times of up to 3 mo. In no cases could we observe the formation of high polymers in these cases, though control experiments with methyl methacrylate and isopropyl acrylate readily gave polymers under the same conditions.

We suggest that the explanation for this lack of reactivity by the more heavily substituted monomers is that their dimers easily can form stable cyclobutane ring systems (I) of the general type proposed by Holden and Hapworth to account for the formation of "abnormal" Michael reaction products. The cyclobutane ring system in (I) is stabilized by the many



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bulky substituents on the ring and represents therefore a pseudo-termination of the chain reaction. The Michael reaction, therefore, usually stops with the addition of one acceptor molecule. This explains the observed dimerisation of crotonic esters. Acrylates and methacrylates do not have substituents on all the carbon atoms in the ring and the ring form (I) is thus not stabilized with the result that polymerization takes place. The formation of the oxidized azetidine ring system required for the formation of similar pseudo-terminated ends in the case of the unsaturated nitro compounds is rather unlikely as such ring formation destroys the resonance possibilities of the nitro group; hence, the easy polymerization of such monomers.

Similar six-membered ring formation to give pseudo-terminated polymer ends has earlier been proposed by Glusker and co-workers to account for the very broad molecular weight distribution obtained by the anionic polymerization of methyl methacrylate (16).

EXPERIMENTAL

Purification of Materials

Solvents and liquid monomers were distilled over calcium hydride before use. Solid monomers were dried over phosphorous pentoxide in vac-

uum. Butyllithium was supplied by the Foote Mineral Co., in pentane-heptane (1:2) solution (1.5M). Isobutylmagnesium bromide in toluene was prepared by standard methods. Sodium methoxide was supplied by Fisher Scientific Co. 1-Nitro-propene (11), ethyl-4-methoxycinnamate (17), ethyl-α-acetyl-4-methoxycinnamate (18), ethyl-α-acetylcinnamate (18), ethyl-α-acetylcrotonate (19), ethyl-α-cyano-4-methoxycinnamate (20), ethyl-2-cyano-4-methylpent-2-enoate (20) were all prepared by the methods indicated. The other reagents were commercially available.

The polymerization methods used are illustrated by the following examples:

Polynitrostyrene. Five milliliters 3.3M isobutylmagnesium bromide in toluene was added under nitrogen at room temperature with stirring to 50 ml. dry, freshly distilled dimethyl sulfoxide. Some heat of reaction was observed (21). Ten grams β-nitrostyrene in 35 ml. dimethyl sulfoxide was added with stirring over 15 min. Polymer started to settle out after 5 min. The suspension was stirred for 5 hr. then poured into methanol containing 3 ml. hydrochloric acid. The polymer was isolated as a fine powder by filtration in essentially 100% yield. The polymer was insoluble in all solvents investigated.

Poly-1-nitropropene. Three milliliters 1.5N butyllithium in 50 ml. dry toluene was allowed to react for 3 hr. with 5 ml. 1-nitropropene as described above to give an opaque, viscous solution. Isolation of the polymer in the fashion as above gave 0.6 g. of a solid, amorphous material which only partially redissolved in hot dimethylsulfoxide. In agreement with earlier observations, 1-nitropropene gave solid material in high yields when shaken with saturated solution of sodium bicarbonate.

Attempted Polymerization of Ethyl α-acetyl-4-methoxycinnamate

Five milliliters of ethyl α-acetyl-4-methoxycinnamate in 15 ml. toluene was flushed with nitrogen, and the solution cooled to $-60°C$. Three ml. of 1.5N butyllithium solution was added, and the stirring continued one hour, when another portion of 3 ml. butyllithium was added. The solution was stirred for another hour, and then poured into 100 ml. methanol containing 1 ml. conc. hydrochloric acid. The clear solution was diluted with water and extracted with chloroform, and the extract evaporated. The residue showed the same IR spectrum as the starting material.

Attempted Polymerization of Ethyl crotonate

Two and one-half milliliters of toluene, 2.5 ml. ethyl crotonate and 1 ml. 1.5N butyllithium solution was mixed and sealed in a reaction tube under vacuum and left at $-20°C$. for 3 mo. A gel was formed, but only traces of nonvolatile products could be isolated after neutralization of the reaction mixture. In a similar experiment, termination was done with

CH_3I. No polymer was formed here either.

Attempted Polymerization of Ethyl cinnamate

Five milliliters of ethyl cinnamate and 2 ml. 1.5N butyllithium solution was sealed in a tube under vacuum and left at −20°C. for 3 mo. Only traces of nonvolatile products could be isolated after neutralization.

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References

(1) Michael, A., Am. Chem. J., 9, 112 (1887).

(2) Bergmann, E. D., D. Ginsburg, and R. Pappo, Org. Reactions, 10, 179 (1959).

(3) Schuerch, C., Ann. Rev. Phys. Chem., 13, 195 (1962).

(4) Garrett, B. S., W. E. Goode, S. Gratch, J. F. Kincaid, C. L. Levesque, A. Snell, J. D. Stroupe, and W. H. Watanabe, J. Am. Chem. Soc., 81, 1007 (1959).

(5) Goode, W. E., F. H. Owens, R. P. Fellmann, W. H. Snyder, and J. E. Moore, J. Polymer Sci., 46, 317 (1960).

(6) Priebs, B., Ann., 225, 319 (1884).

(7) Meisenheimer, J., and F. Heim, Ann., 355, 260 (1907).

(8) Nash, J. L., "Polymerization Studies of Unsaturated Derivatives of β-Nitrostyrene," thesis, Univ. of Florida, 1953.

(9) Schmidt, E., and G. Rutz, Ber., 61, 2142 (1928).

(10) Buckley, G. D., and C. W. Scaife, J. Chem. Soc., 1947, 1471.

(11) Topchiev, A. V., V. P. Alaniya, and Z. A. Morakova, Dokl. Akad. Nauk SSSR, 131, 1359 (1960), (Engl. transl. Chem. Sect. p. 433).

(12) Cope, A. C., U.S. Patent, 2,222,455 (1940).

(13) Peckmann, H. V., Ber., 33, 3323 (1900).

(14) German Patent, 927 384 (1955).

(15) Holden, N. E., and A. Lapworth, J. Chem. Soc., 1931, 2368 (cf. ref. 2, p. 191).

(16) Glusker, D. L., I. Lysloff, and E. Stiles, J. Polymer Sci., 49, 315 (1961).

(17) Horeau, A., Bull. Soc. Chim. France, 15, 414 (1948).

(18) Horning, E. C., J. Koo, M. S. Fish, and G. N. Walker, Org. Syn., 31, 56 (1951).

(19) Knoevenagel, E., Ber., 31, 730 (1898).

(20) Popp, F. D., J. Org. Chem., 25, 646 (1960).

(21) Oda, R., and K. Yamamoto, J. Org. Chem., 26, 4679 (1961).

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CONFIGURATIONAL EFFECTS OF ACIDS IN GEL-FORMATION OF POLYVINYL ALCOHOL INDUCED BY γ-RAY IRRADIATION

Effects of gamma-ray irradiation on aqueous solution of polyvinyl alcohol (PVA) have been investigated both theoretically (1) and experimentally. Berkowitch et al. (3) found an internal linking by γ-ray irradiation in dilute PVA solution. Danno (2) observed that the results of irradiation depend on the conditions of atmosphere and concentration of the solution. PVA is degradated when it includes oxygen, and is gelated when oxygen-free. In the solutions of higher concentrations, PVA is gelated, and is not in those of lower concentrations. The critical concentration to form gel was reported as 0.36 weight-%.

This letter presents the results of an investigation where PVA solutions are irradiated in acid solutions with oxygen-free atmosphere.

Experimental

PVA with a degree of polymerization of ca. 1740 was dissolved in hot water and several kinds of acids were added as shown in Table I. Acids used were acetic, hydrochloric, nitric, perchloric, sulfuric, boric, and phosphoric. Solutions were deoxygenated by passing highly pure nitrogen gas, and sealed in glass test tubes. The samples were irradiated by ^{60}Co γ-ray at 25°C. Irradiation was made at Tokyo Institute of Japanese Association for Radiation Research on Polymers, Komagome, Tokyo. The source intensity is 500 curies and dose rate 6.7×10^4 roentgens/hr. Two series of samples were prepared, one with a PVA concentration of 0.4% which is higher than the critical concentration and the other of 0.2% which is lower.

Because of salt effects, viscosity of the solution was not measured exactly and the change in degree of polymerization was not obtained. The change in appearance of solution is described in Table I. In cases of CH_3COOH, HCl, HNO_3, and H_3BO_3, no gelation was observed in either the 0.2 and 0.4% PVA solutions. In 0.4% solutions small bubbles were suspended in the solutions.

Whereas in all solutions of $HClO_4$, H_2SO_4, and H_3PO_4 gels were formed at every concentration, even below the critical concentration. The dose for incipient gelation decreases as the concentration of the acids increases, but optimum concentrations of the acids seemed to exist.

When we used pentaerythritol as an alternate of anions with tetrahedral structures, no gelation was observed by γ-ray irradiation except the formation of small bubbles. It may be concluded that an organic compound

TABLE I*

Effects of Several Acids on Irradiation-Induced PVA Gel Formation

Acids	Concentration, N	Irradiation time, hr. 6	12	18	24	Dose for incipient gelation ($\times 10^5$ rads)
		(1) 0.2% PVA				
CH_3COOH	0.08, 0.2, 0.5	un.	un.	un.	un.	–
HCl	0.08, 0.2, 0.5	un.	un.	un.	un.	–
HNO_3	0.08, 0.2, 0.5	un.	un.	un.	un.	–
$HClO_4$	0.08	un.	un.	un.	tu.	16
	0.2	sl.tu.	tu.	gl.	gl.	4
	0.5	un.	sl.tu.	tu.	gl.	8
H_2SO_4	0.08	un.	tu.	gl.sp.	gl.sp.	8
	0.2, 0.5	sl.tu.	tu.	gl.	gl.	4
H_3BO_3	0.08, 0.2, 0.5	un.	un.	un.	un.	–
H_3PO_4	0.08	un.	sl.tu.	gl.	gl.sp.	8
	0.2	sl.tu.	gl.	gl.sp.	gl.sp.	4
	0.5	un.	tu.	gl.	gl.sp.	8

(2) 0.4% PVA

CH_3COOH	0.08, 0.2, 0.5	un.	un.	un.	un.	–
HCl	0.08, 0.2, 0.5	un.	un.	un.	un.	–
HNO_3	0.08, 0.2, 0.5	un.	un.	un.	un.	–
$HClO_4$	0.08	tu.	gl.	gl.	gl.sp.	4
	0.2	tu.	gl.	gl.	gl.	4
	0.5	sl.tu.	tu.	tu.	gl.	4
H_2SO_4	0.2	tu.	gl.	gl.	gl.	4
H_3BO_3	0.08, 0.2, 0.5	un.	un.	un.	un.	–

*Abbreviations: un., unchanged; sl.tu., became turbid slightly; tu., became turbid; gl., gelated; gl.sp., gel was separated.

with a tetrahedral structure cannot produce effects similar to those of the tetrahedral anions.

Furthermore, in alkaline solutions of NaOH or KOH, gels were not formed, regardless of concentrations of both alkalies and PVA.

In the case of $CuSO_4$, the polymer was gelated by sulfate anions, and cupric cations were reduced to form a reddish precipitation.

We point out here that the tetrahedral anions, such as ClO_4^-, SO_4^{2-}, and PO_4^{3-}, are helpful to irradiation-induced gel formation, and assume that the coordination of these anions is suitable to produce a preferable alignment of PVA.

As is well known, gels of monodiol or didiol type comlexes are formed by simple addition of boric acid or borax to PVA solution (4). This is another case of a steric alignment of PVA molecules.

References

(1) Saito, O., J. Phys. Soc. Japan, 13, 1465 (1958); 14, 798 (1959).

(2) Danno, A., ibid., 13, 722 (1958).

(3) Berkowitch, J., A. Charlesby, and V. Desreux, J. Polymer Sci., 25, 490 (1957); 31, 256 (1958).

(4) Deuel, H., and H. Neukom, Makromol. Chem., 3, 13 (1949).

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